



Correlations between oxygen activation and methane oxidation over Pd/ γ -Al₂O₃ catalysts prepared by nitrite method

Satu Ojala^{a,*}, Nicolas Bion^b, Alexandre Baylet^{b,1}, Mehrad Tarighi^b, Riitta L. Keiski^a, Daniel Duprez^b

^a Laboratory of Mass and Heat Transfer Process, University of Oulu, POB 4300, 90014 University of Oulu, Finland

^b Laboratoire de Catalyse en Chimie Organique (LACCO), Université de Poitiers/CNRS, 4 rue Michel Brunet, 86022 Poitiers – Cedex, France

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ABSTRACT

In this work the oxygen activation properties and methane oxidation activities of Pd/Al₂O₃ catalysts prepared by the nitrite-complex method are investigated. The effects of altering the preparation procedure and *in-situ* pre-treatments are considered. Based on the results, correlations between isotopic exchange and methane oxidation activities are drawn. Even if Pd/Al₂O₃ catalysts have typically a low activity in oxygen activation, it was found, that reductive *in-situ* pre-treatment of the catalyst significantly enhances the activity of oxygen activation studied by isotopic exchange and equilibration experiments. In addition, both equilibration and exchange take place on the pre-oxidized catalyst, whereas mainly equilibration occurs on the pre-reduced catalyst. The catalyst sample that was reduced prior to washing in the preparation stage showed to be most active in both cases, in isotopic oxygen exchange and in methane oxidation. The explanation to the enhanced activity is suggested to be originated from more easy reducibility of palladium.

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1. Introduction

Palladium is widely used as a catalyst in automotive exhaust gas converters together with platinum [1,2], but also in catalytic incineration applications [3]. Palladium catalysts have found their place especially in methane oxidation applications where they have been proven to be very active, usually more active than the other noble metal catalysts [4]. It is often suggested that the active form of palladium in methane oxidation at rather low temperatures is crystalline PdO, but at higher temperatures metallic palladium may be active as well [5]. There are also results revealing that the most active form of a supported palladium catalyst is a PdO layer on the top of the Pd metal core when palladium is supported on ZrO₂ [6]. At low temperatures, the methane oxidation activity was even more enhanced, if slight amount of metallic Pd was created to the catalyst surface, since metallic Pd can dissociate CH₄ more easily than PdO. Furthermore Su et al. state that crystalline PdO is more easily reduced than amorphous PdO. The downside of the observation was, that in steady state conditions Pd was reoxidized rather fast and therefore the initial higher activity was also reduced [7]. The mechanism of methane oxidation over PdO is suggested to go through the redox or Mars–van Krevelen type of

mechanism, which is affected by water inhibition. However, oxidation over metallic Pd is suggested to be affected by competitive adsorption of methane and oxygen [5,8–11]. Very recently Cortés et al. [12] published Monte Carlo simulations that use mechanism with two independent adsorption sites for methane and oxygen adsorption suggested by Fujimoto et al. [13]. The model interprets the experimental results of methane oxidation over PdO_x well showing the possibility of existence of two different adsorption sites in the case of PdO_x. When it comes to other catalyst parameters than Pd–PdO transformation, Castellazzi et al. [14] have studied the effect of dispersion and loading on the redox behavior of palladium catalysts supported on alumina in methane oxidation. It was seen in their studies that catalytic activity is decreased for higher dispersion, which was suggested to be related to a lower reducibility of smaller PdO particles. In addition, there exist rather recent results [15] showing that reduction of PdO depends strongly also on the reducing agent. For example reduction of PdO by H₂ occurs at lower temperature than reduction by CH₄.

The oxygen activation on Pd-catalysts has been seen to be lower than over the other noble metals [16]. This difference cannot be explained by different adsorption energies of oxygen on metallic Pd, Rh or Pt, since they are very similar [17,18]. From these adsorption energies, it can be calculated that the temperature of decomposition of corresponding oxides is near 800 °C. Based on the experimental studies of Baylet et al. [15] the decomposition of PdO occurs only above 700 °C in inert conditions. Thus, one can expect that the exchange or equilibration should occur on the surface of PdO at lower temperatures. The difference between the rate

* Corresponding author. Tel.: +358 8 553 2318; fax: +358 8 553 2304.

E-mail address: satu.ojala@oulu.fi (S. Ojala).

¹ Present address: Céramiques Techniques Industrielles, 382 avenue du Moulinas, 30340 Salindres, France.

of exchange of the above-mentioned noble metals can be due to the fact that PdO is quite stable and does not easily change oxidation state of a metal. This is not the case for example with Rh that can easily create new phases over a wide range of oxygen vacancies. Based on the earlier studies, it is believed that Pd oxidation starts with rapid formation of oxygen monolayer at rather low temperature (-73°C), which is the onset temperature for oxygen dissociative adsorption on Pd [6]. Bulk oxidation starts then later at above 200°C , which is proposed as a starting temperature of dissociative adsorption of O_2 on Pd [19]. The phenomena related to palladium reduction and oxidation are important in the oxidation reactions, since they are related to the activity of the catalyst. The oxygen activation and mobility can be studied by isotopic exchange and equilibration experiments.

In general, there are three types of exchange of dioxygen on oxide catalysts, namely, the homoexchange or isotopic equilibration, the simple heteroexchange and the multiple heteroexchange. The difference between equilibration and exchange is, that equilibration occurs between two adsorbed molecules originating from a gas-phase whereas exchange involves also participation of oxygen from a solid [20]. Equilibration experiments (homoexchange) give information about the nature and surface area of metal particles, and the experiments are normally carried out with equimolar mixtures of a certain gas molecule and its isotopic counterpart. Heteroexchange, or simply, isotopic exchange experiments, can be used to reveal, e.g. diffusion coefficients on the surface of catalysts. The isotopic exchange experiments can be carried out with pure isotopic gas. When separating between the isotopic exchange and equilibration, α_g -value, namely the value giving the atomic fraction of labeled atom in the gas phase, is very useful value. If α_g -value remains approximately constant during the equilibration experiment, it means that only equilibration reaction occurs. If α_g -value decreases, it means that exchange occurs simultaneously during the equilibration experiment [16]. Isotopically labeled molecules can also be used in reaction mechanistic studies. For example, it can be concluded from isotopic experiments, which oxygen (i.e. oxygen from the gas phase or oxygen from catalytic surface) takes part in the catalytic oxidation reactions. Even if the isotopic oxygen exchange is a mature methodology, there are not many studies available concerning the relations of the exchange activity on oxidation activity of the catalysts.

This study is carried out to understand the phenomena related to the oxygen activation properties of palladium by isotopic exchange and equilibration experiments. The aim is to discover the reasons why the activity of palladium is generally not as good as the activity of other noble metals in oxygen activation. For this purpose Rh/ Al_2O_3 was used as a reference material, since it is known to be very active in oxygen activation compared with other noble metals. In this study, the effects of different preparation procedures (when using the nitrite-complex preparation method) and the *in-situ* pre-treatment of the catalyst before the experiment are taken into account. Furthermore, the correlations between methane oxidation and oxygen activation properties of palladium, and the effect of the presence of gas-phase CO_2 to oxygen activation are considered, since it will be present in a gas mixture when methane is oxidized and there are previous indications [21] that it has an influence on oxygen activation.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation with the Pd-nitrite complex formation explained in Ref. [22]. The γ - Al_2O_3 used as a support material had specific area of $204\text{ m}^2\text{ g}^{-1}$ and

it was provided by Axens. This catalyst preparation method should allow high dispersion of Pd^0 particles on the gamma-alumina support and it is based on avoiding the strong interactions with the support during the preparation. Prior to impregnation NaNO_2 and $\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ aqueous solutions were mixed. The pH of solution was adjusted by an addition of concentrated NaOH in order to keep it always on the level >1 . The quantity of NaNO_2 was calculated so that the ratio NO_2^-/Pd was 4. The solution concentration was calculated to result in a palladium loading of 1 wt.%.

The solution containing Pd-nitrite was added to the pre-calcined gamma-alumina (700°C , 4 h, $1\text{ dm}^3\text{ air h}^{-1}\text{ g}_{\text{cat}}^{-1}$) under agitation. The final product was let to 'mature' overnight in a covered beaker before further treatment. Drying and calcination of the catalyst was carried out by drying on a sand bed during 9 h and in a furnace at 120°C overnight followed by calcination at 200°C for 2 h in dry air flow ($1\text{ dm}^3\text{ h}^{-1}\text{ g}_{\text{cat}}^{-1}$). Two parts of the prepared catalyst (called as Pd-dry) were further treated by washing and by reduction followed by washing. Washing of the catalyst was carried out in order to remove the residual Na, which may affect the catalyst performance. Washing was done 5 times with ultra pure water. Reduction prior to washing of the third part of the catalyst was done at 200°C for 2 h under $1\text{ dm}^3\text{ h}^{-1}\text{ g}_{\text{cat}}^{-1}$ of hydrogen flow. These samples are called as washed (Pd-w), and reduced and washed (Pd-rw) sample.

2.2. Catalyst characterization

The catalysts were characterized by H_2 chemisorption, BET, BJH, ICP and TEM-EDX. The specific surface areas and pore sizes of the catalysts were determined with BET and BJH method, respectively, from nitrogen adsorption at -196°C with a Tristar 3000 Micromeritics apparatus. Prior to the measurement, the sample was pretreated at 250°C under vacuum for 4 h and then cooled in vacuum during 2 h in order to eliminate the adsorbed species. The measurements of dispersion were carried out with H_2 pulse chemisorption at 80°C . Prior to the chemisorption the catalysts were reduced for 1 h in hydrogen flow ($30\text{ cm}^3\text{ min}^{-1}$) and then purged with argon ($30\text{ cm}^3\text{ min}^{-1}$) during 3 h at 400°C .

Pd and Na contents of the catalysts were determined by elemental analysis using a Perkin Elmer Optima 2000 DV inductive coupled plasma-optical emission spectrometry (ICP-OES) system. Prior to measurements, samples were prepared using a microwave assisted acid (a mixture of HCl and HNO_3) digestion method. The localization of Na and Pd particle sizes were evaluated by transmission electron microscopy (TEM) measurements by a Jeol 2100 UHR apparatus, with a 0.19 and 0.14 nm punctual and linear resolution, respectively, equipped with a LaB.6 filament. Energy dispersive X-ray (EDX) analysis was performed for local chemical analysis (in TEM mode). The X-rays emitted from the samples upon electron impact were collected in the range 0–20 keV.

2.3. Isotopic exchange experiments

Isotopic oxygen exchange experiments were carried out in a closed-loop reactor system. A recirculating pump was used in order to avoid any diffusion and mass transport effects in the gas phase that affect partial pressures of different isotopomers measured by mass spectrometry (Pfeiffer Vacuum). The used reactor system is described in more detail in Refs. [21,23].

The needed amounts of reacting gases used in the experiments ($^{18}\text{O}_2$, $^{16}\text{O}_2$, CH_4 ; isotopic gases supplied by Isotec with 99.3 ^{18}O atom % purity for $^{18}\text{O}_2$) were introduced into the reactor system after which the system inlet was closed. During the introduction of the gases into the system, the entry of the actual reactor cell was closed. After introduction, the 'starting levels' of the reacting gases were measured by mass spectrometry, the reactor inlet was opened and reaction initiated. The total pressure of the reacting gases was

kept constant (50 mbar) in all the experiments. In isotopic exchange experiment, only $^{18}\text{O}_2$ was used. In equilibration an equimolar mixture of $^{18}\text{O}_2$ and $^{16}\text{O}_2$ was used. The methane oxidation experiment with labeled oxygen was carried out with 1:2 mixture of gas. After opening the reactor cell, the amounts of the gas-phase compounds were followed during 20–30 min at reaction temperature.

The catalysts were pre-treated prior to the experiments in different ways: the catalyst sample was either oxidized in O_2 flow (during 15 min) or reduced in H_2 flow (during 15 min) *in-situ* at the same temperature where the experiment was carried out. After the pre-reduction or pre-oxidation, the catalyst was evacuated for 30 min at reaction temperature. Reaction temperatures used in the experiments were 200, 300, 400 and 500 °C.

The existence of the surface carbonates was verified by FTIR-measurements (Bruker Equinox 55, equipped with MCT detector). In these experiments catalyst pellet was compressed as a wafer and installed into a tailor-made IR-cell that was possible to heat up to 500 °C. In the experiment, the catalyst sample was heated up to 400 °C in vacuum, after which the reductive and oxidative pre-treatment similar to the pretreatment used during isotopic experiments was carried out. IR-spectra were collected before the pre-treatment (in vacuum), during reduction, after reduction (in vacuum), during oxidation and after oxidation (in vacuum).

The calculation of the reaction rate for the isotopic exchange and equilibration experiments was carried out based on the initial-rate method. In this calculation the tangent at the very beginning of the concentration vs. time curve for exchanged molecule is used to determine the rate of the reaction. For example, for isotopic exchange the rate equation final form is following:

$$r_e = -N_g \frac{d\alpha_g}{dt} \quad (1)$$

$$\frac{d\alpha_g}{dt} = \frac{1}{P_0} \left[2 \frac{dP_{*X*X}}{dt} + \frac{dP_{*XX}}{dt} \right] \quad (2)$$

where α_g is atomic fraction of *X in gas phase at time t , P_0 is total pressure, P_{*X} is partial pressure of a compound X or *X , X is atom of ^{16}O and *X is atom of ^{18}O . For the derivation of the equations and additional information please see Ref. [16].

2.4. Methane oxidation

The methane oxidation experiments were carried out in a continuous flow tubular reactor. The analysis was done by Varian 9000 GC equipped with FID detector and Porapak packed column. The reaction mixture contained nitrogen, oxygen and methane (89.5/10/0.5 vol-%) with the total flow of 200 $\text{cm}^3 \text{min}^{-1}$. The catalyst packing contained 250 mg SiC and 25 mg of catalyst. The experimental procedure consisted of series of light-off tests done periodically by heating and cooling the reactor. Between the heating and cooling stages of the experiment the stability of the catalyst was followed at constant temperature. The experiments were carried out starting from room temperature up to 400 °C with a heating/cooling rate of 5 °C min^{-1} . The duration of the stability test at the highest temperature was 30 min. The procedure was carried out twice with all three catalysts. Before the experiments, the catalysts were calcined at 500 °C.

3. Results

The fact that palladium catalysts are not very active in isotopic oxygen exchange is unfortunate, since isotopic oxygen exchange can be used to deepen the knowledge on the oxygen activation and oxidation processes where palladium is very often used. Therefore, we wanted to find out what was the cause of this low activity and if the oxygen exchange activity of a palladium catalyst could be

enhanced by some way. To achieve the goal, we tested different preparation procedures and different *in-situ* pre-treatments of the catalyst as well as different mixtures of reacting gases during isotopic experiments. It has been noticed before that the activity of alumina-supported Pd is low over catalysts prepared from chloride or nitrate precursors. Chloride ions are generally considered as a strong inhibitor of oxygen exchange on most of the metals [16,24]. The fact that the Pd-catalyst prepared from nitrate precursor also gave very poor exchange activity showed that chloride ions were not responsible, alone, for this feature of Pd. Therefore, a new preparation technique using Pd-nitrite was employed. It was proven by Benkhaled et al. that this method gives well-dispersed catalysts [22] with very good activity in hydrogenation reactions [24]. To our knowledge, the Pd-catalysts prepared with the nitrite method are used for the first time for oxidation reactions. Three different catalyst samples were prepared as described in Section 2. The difference in the samples was the washing-stage after the dry-impregnation. Part of the catalysts was washed with water (Pd-w) and part of the catalysts was reduced before washing (Pd-rw). As comparison, one part of the catalysts was not washed nor reduced (Pd-dry). Prior to isotopic experiments, all these three samples were then either pre-oxidized or pre-reduced *in-situ*. The characterization results of the catalysts are presented in Table 1.

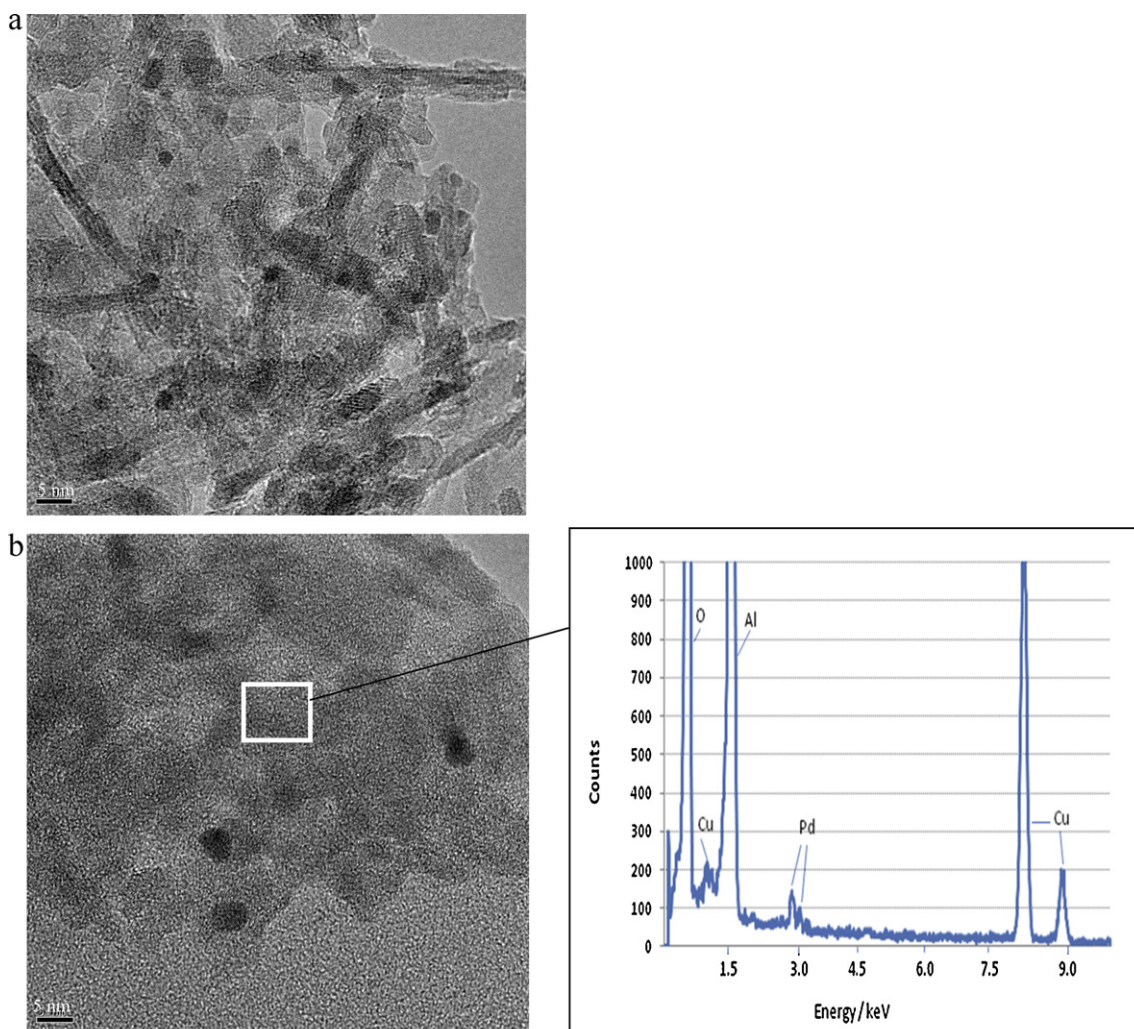
The characterization results show in general, that washing with water can be used to reduce the residual Na amount in the catalyst. It seems that reduction before washing somehow stabilizes sodium, and it is not removed as easily as from the non-reduced catalyst. The further treatments also seem to increase the specific surface area of the catalyst. The effect of (only) washing on the BET value is somewhat insignificant, but the reduction of the catalyst before washing increases the BET value significantly. This cannot be explained by possible opening of pores during the Na removal, since the amount of Na is higher in the Pd-rw catalyst than in the Pd-w catalyst. The treatments of the catalysts seem to decrease the dispersion of palladium measured by chemisorption. However, TEM measurements showed that the particle size of Pd in all the catalysts is very similar. Differences are seen between the Pd-dry and Pd-rw catalysts where Pd is either in clusters (Pd-dry) or in a well-dispersed form (Pd-rw). The clusters observed in the Pd-dry catalyst have a cluster size of about 100 nm containing hundreds of Pd-particles. The particles are, however, not adhered together, since chemisorption measurements show good accessibility of H_2 . In the case of the Pd-w catalyst the situation is more complicated, since TEM measurement show the presence of few ~4 nm particles, but also EDX shows the presence of Pd in places where it cannot be detected undoubtedly (see Fig. 1a and b). In this case the presence of <1 nm particles is possible. About the location of Na, we can be sure only in the case of the Pd-dry catalyst, where Na is located close to the Pd clusters. In the case of Pd-w, Na was not observed probably due to a small amount of Na present in the sample (see ICP results in Table 1), and in the case of Pd-rw, it was observed based on EDX analysis, but it was not visually seen. According to the BJH measurements, the pore size of the Pd-rw catalyst is slightly smaller than in the other two catalysts and the total pore volume is higher. XRD measurements show that the crystallite size of gamma-alumina in the Pd-rw catalyst is somewhat smaller than with the other two catalysts, which was also proven by TEM, however, the difference is not remarkable.

3.1. Methane oxidation results

The methane oxidation activities of the catalysts were tested in experimental conditions explained in detail in Section 2.4. The results showed, in general, that the most active and stable catalyst was Pd-rw. The results of repeated methane oxidation cycles for Pd-rw are shown in Fig. 2.

Table 1
Characterization results of the catalysts.

	Na (wt.%)	Pd (wt.%)	BET (m ² g ⁻¹); calc. 500 °C	D (%); calc. 500 °C	Particle size (nm)	Morphology
Pd-dry	1.097	0.86	183	35.5	2–3	Clusters
Pd-w	0.378	0.86	188	26.1	<1 and 4	Dispersed
Pd-rw	0.615	0.87	230	16.3	2–3	Dispersed

**Fig. 1.** (a) TEM image of the Pd-rw (reduced and washed) catalyst; (b) TEM image of the Pd-w catalyst and EDX analysis from the zone where Pd cannot be visually observed.

During the repeated cycles of methane oxidation, differences between the catalyst performances were clearly observed. Between the heating and cooling cycles, the catalysts were kept in a constant temperature (400 °C) during 30 min. This gave us better possibility to observe the stability of the catalysts (see Fig. 2). As mentioned, the activity and stability of Pd-rw catalyst was the highest. The repeated experiments gave rather similar results as can be seen in Fig. 3. In general, the activity and stability of the Pd-w and Pd-dry catalyst were significantly lower than that of the catalyst Pd-rw. The catalysts Pd-w and Pd-dry showed some activation during

the first constant temperature phase that was more pronounced with the catalyst Pd-dry having the cluster-like form of Pd particles. However, especially the Pd-dry catalyst started to lose its activity already during the second heating cycle. After evaluation of the activities of the catalysts during the different cycles we observed that the most representative and comparable values for catalyst activities are those that were gotten in the beginning of the second cooling cycle. These conversion values and the corresponding TOF-values together with the minimum light-off temperatures observed are presented in Table 2. In the TOF calculation first order

Table 2
Comparison of the catalysts in methane oxidation.

Catalyst	Light-off temperature (T_{50}) (°C)	Conversion at 395 °C second experimental run (%)	TOF at 395 °C first experimental run (s ⁻¹)
Pd-dry	~430 ^a	27	0.30
Pd-w	404	35	0.57
Pd-rw	380	54	1.62

^a Not reached at test conditions, estimated graphically.

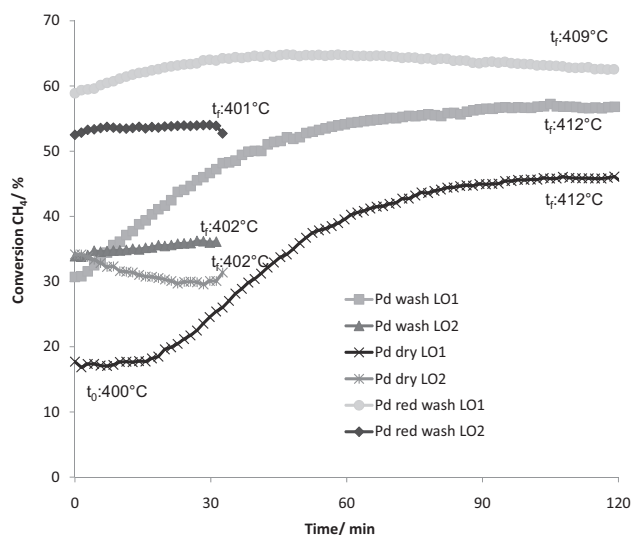


Fig. 2. Stability of the tested catalysts in methane oxidation. Isothermal experiment at 400 °C after every light-off test (H denotes heating, C cooling, 1 and 2 first and second experimental cycles).

reaction kinetics were applied for correction of the values. When these results are compared with earlier methane oxidation studies [5,25], one can observe that the activities of the prepared catalysts are at the same level or slightly better than the activities of previously developed palladium catalysts for methane oxidation.

3.2. Isotopic exchange results

The isotopic exchange and equilibration experiments were carried out at several temperatures (200 °C, 300 °C, 400 °C and 500 °C). In general, neither the oxygen exchange nor the equilibration over Pd/γ-Al₂O₃ was significant at 200 °C and 300 °C. Therefore, the rates of isotopic oxygen exchange (for *in-situ* pre-reduced catalysts) are shown in Fig. 4 only at the temperatures of 400 °C and 500 °C. For comparison, the figure shows also the oxygen exchange rate of gamma-alumina supported rhodium, which is a very good oxygen exchanger, and in fact, it is the most active of the noble metals in

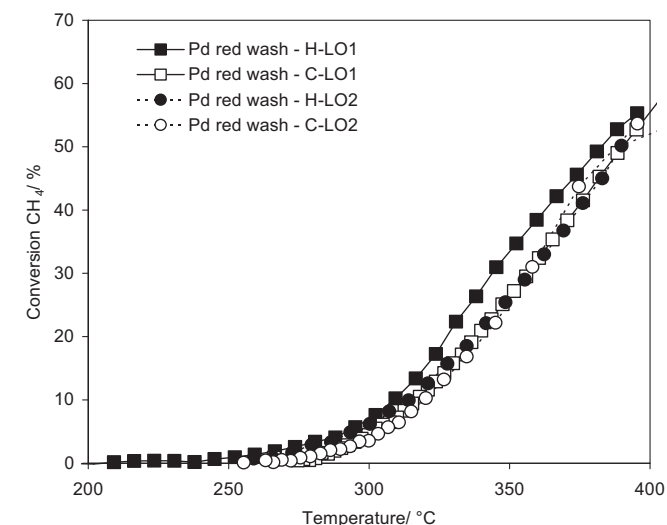


Fig. 3. Results of methane light-off test cycles over the Pd-rw (reduced and washed) catalyst (H denotes heating, C cooling, 1 and 2 first and second experimental cycles, respectively).

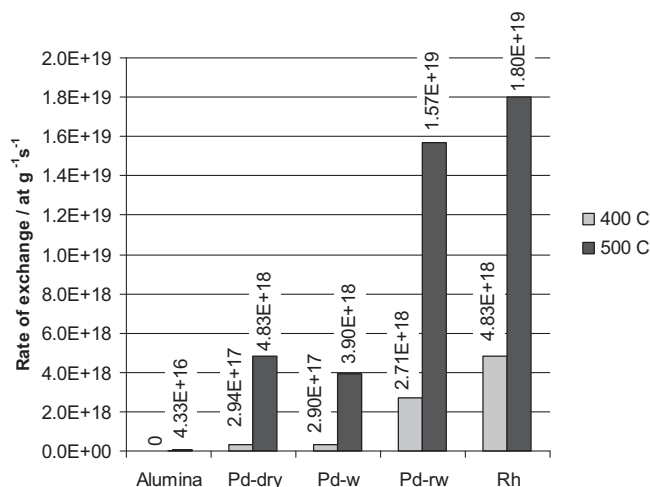


Fig. 4. Oxygen exchange rates over the *in-situ* pre-reduced catalysts at 400 °C and at 500 °C.

oxygen exchange reaction [16]. Fig. 4 indicates that the most active catalyst of the prepared palladium catalysts is Pd-rw, which is surprisingly very close to the activity of Rh/γ-Al₂O₃. However, the rate of exchange is calculated by the initial rate method, and when the total numbers of exchanged atoms are considered, one will find out that the values for Rh/γ-Al₂O₃ are significantly higher than that for the Pd-rw catalyst.

In addition to the preparation procedure and temperature, the isotopic exchange rate is also dependent on the *in-situ* pre-treatment that is shown in Table 3. Pre-reduction of the catalysts results in higher isotopic exchange rates.

Numbers of exchanged atoms at time $t = 12$ min are presented in Table 4. In general, it seems that a higher number of oxygen can be exchanged over a pre-reduced catalyst than a corresponding pre-oxidized catalyst. This is especially important in the case of the Pd-rw catalyst at 500 °C. The value for oxygen atoms of PdO in the tested catalysts is 4.9×10^{19} at g⁻¹ catalyst. The values in Table 4 show that at time $t = 12$ min, only the Pd-rw catalyst at 500 °C has exchanged all the oxygen atoms from PdO and oxygen mobility between γ-Al₂O₃ and PdO can be confirmed.

3.3. Isotopic equilibration results

The results of the equilibration experiments with ¹⁸O₂ and ¹⁶O₂ show a similar trend compared to that of the isotopic exchange experiments. Table 5 shows the equilibration rates over the tested catalysts at 500 °C. The equilibration rates over the Pd-dry and Pd-w catalyst samples at 400 °C are insignificant especially over the *in-situ* pre-oxidized catalysts. However, equilibration occurs over the Pd-rw catalyst at 400 °C in both cases: after *in-situ* pre-reduction and after *in-situ* pre-oxidation. The equilibration activity is increased at 500 °C for all the catalysts and the rate of equilibration at 500 °C is higher for the pre-reduced catalysts, as it was in the case of isotopic exchange.

The interesting aspect between pre-oxidized and pre-reduced samples is that, after pre-oxidation of Pd-rw (at 400 °C and at 500 °C) and Pd-w (at 500 °C), the value of ¹⁶O₂ does not decrease at the same ratio that ¹⁸O₂ and ¹⁶O¹⁸O values change. The results show that production of gas-phase ¹⁶O₂ is almost at the same level than the consumption of gas-phase ¹⁶O₂. It means that isotopic exchange occurs together with equilibration on the *in-situ* pre-oxidized catalyst, which is also proved by the α -value that describes the atomic fraction of labeled oxygen in gas-phase. This phenomenon did not occur over the gamma-alumina-support alone

Table 3

Isotopic exchange rates at 400 °C and 500 °C.

Catalyst	$^{18}\text{O}_2$ exchange rates for pre-oxidized catalyst (at $\text{g}^{-1} \text{s}^{-1}$) ($\times 10^{+17}$)		$^{18}\text{O}_2$ exchange rates for pre-reduced catalyst (at $\text{g}^{-1} \text{s}^{-1}$) ($\times 10^{+17}$)	
	400 °C	500 °C	400 °C	500 °C
Pd-dry	0.4	4.2	2.9	48
Pd-w	0.49	10	2.9	39
Pd-rw	25.7	87	27.1	157

Table 4Numbers of exchanged atoms at $t = 12$ min at 400 °C and 500 °C.

Catalyst	Numbers of exchanged atoms for pre-oxidized catalyst (at g^{-1}) ($\times 10^{+19}$)		Numbers of exchanged atoms for pre-reduced catalyst (at g^{-1}) ($\times 10^{+19}$)	
	400 °C	500 °C	400 °C	500 °C
Pd-dry	0.07	0.53	0.35	2.47
Pd-w	0.18	1.5	0.34	2.15
Pd-rw	1.97	2.54	1.61	16.3

Table 5

Isotopic equilibration rates at 500 °C.

Catalyst	Equilibration rates for <i>in-situ</i> pre-oxidized catalyst (at $\text{g}^{-1} \text{s}^{-1}$) ($\times 10^{+17}$)		Equilibration rates for <i>in-situ</i> pre-reduced catalyst (at $\text{g}^{-1} \text{s}^{-1}$) ($\times 10^{+17}$)	
	400 °C	500 °C	400 °C	500 °C
Pd-dry	5.8		63	
Pd-w	9.2		38	
Pd-rw	28		110	

nor over the Pd-dry catalyst. Example of this phenomenon is presented in Fig. 5.

Since both equilibration and exchange occur at 500 °C in certain cases over the tested catalyst, the values presented in Table 5, in those cases, are smaller than they should be, because in the rate calculation only the formation of $^{16}\text{O}^{18}\text{O}$ is taken into account. Therefore, this is one reason why in certain cases the rates for pure exchange experiments are higher than in the case of equilibration experiments (see Tables 3 and 5). However, both the tables show clearly that the activity of the Pd-rw catalyst is much higher than that of the other two catalysts and that the pre-reduced samples are more active than the pre-oxidized ones.

3.4. Methane oxidation with labeled oxygen

The experiments carried out with methane and labeled oxygen ($^{18}\text{O}_2$) over the pre-reduced (15 min in H_2 at reaction temperature) catalyst show that the first oxidation product appearing in the gas-phase is C^{16}O_2 . It appears slightly before $\text{C}^{16}\text{O}^{18}\text{O}$ production starts and it means that methane reacts first with oxygen still available on

the catalytic surface. After C^{16}O_2 , the appearances of other reaction products are noticed (Fig. 6).

The appearance of C^{16}O_2 as the first reaction product before other isotopomers shows that methane oxidation is faster than the exchange of oxygen over the tested catalyst. Later, also the exchange of oxygen (appearance of $^{16}\text{O}^{18}\text{O}$) is observed with the rate slightly superior to the rate of pure exchange. The effect of enhancing exchange rate may be due to the fact, that methane reduces PdO. However, it is important to notice, that during methane oxidation CO_2 exist which means that carbonates, that can improve the exchange of oxygen, will appear on the catalyst surface as well. The observed improved exchange rates observed in the presence of methane can thus be either explained by reduction of PdO or the formation of carbonates.

To observe the effect of Pd^0 more clearly, one methane – $^{18}\text{O}_2$ experiment, where PdO was treated at 700 °C in vacuum and in hydrogen flow and then cooled to 500 °C (in vacuum) before the experiment was carried out. The results showed rapid formation of $^{16}\text{O}^{18}\text{O}$ at the very beginning of the experiment before starting of methane oxidation. In this case, exchange was faster than oxidation of methane. It shows us first of all, the necessity of the presence

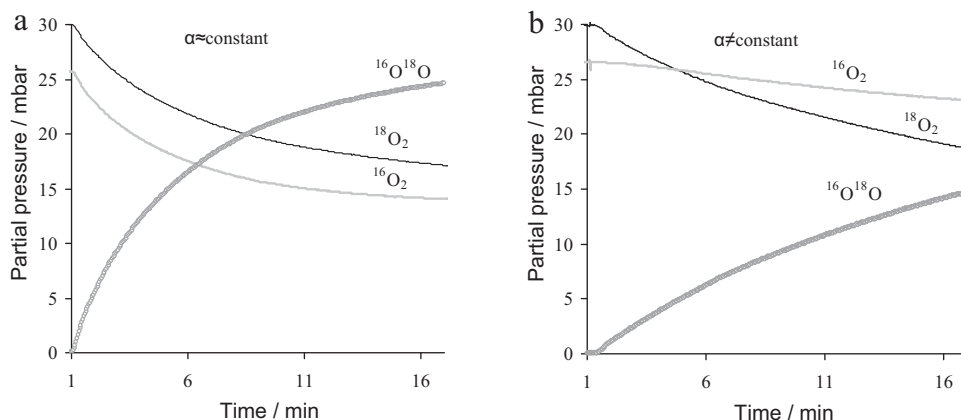


Fig. 5. Equilibration ($^{16}\text{O}_2 + ^{18}\text{O}_2$) results over the pre-reduced (a) and pre-oxidized (b) Pd-rw catalysts at 500 °C. α describes the atomic fraction of labeled oxygen in the gas-phase.

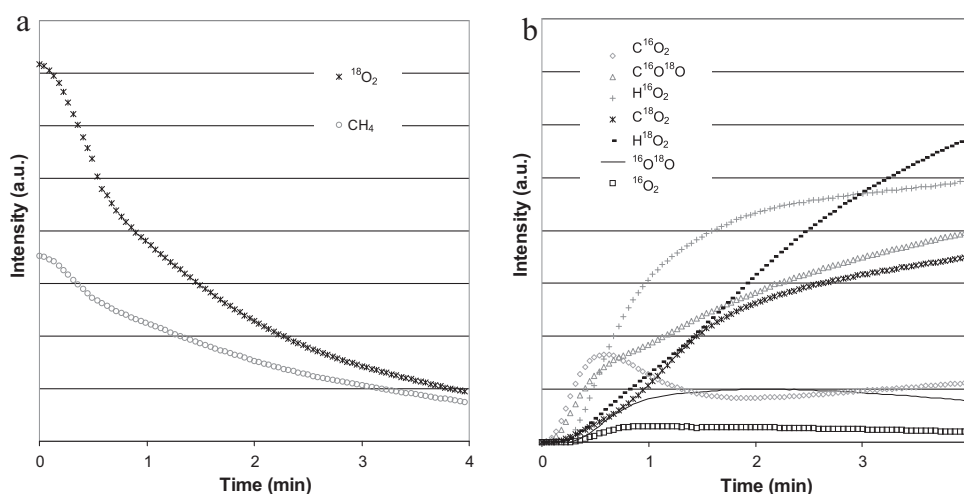


Fig. 6. Results of CH₄ oxidation with labeled oxygen (¹⁸O₂) over the Pd-w catalyst at 500 °C: (a) consumption of the reactants (CH₄ and ¹⁸O₂) and (b) formation of the different isotopomers of CO₂, O₂ and H₂O. Experiment was carried out with 1:2 mixture of CH₄ and ¹⁸O₂.

of PdO in methane oxidation at the used reaction conditions, but also that before methane oxidation occurred, either PdO was not completely decomposed or involvement of oxygen from gamma-alumina support took place. Since the methane oxidation started only after the surface was at least partly re-oxidized, it means that the methane oxidation follows the Mars–van Krevelen-type of mechanism over the tested catalysts.

When the formation of C¹⁶O₂ during the methane oxidation over the tested catalyst is studied in more detail (Fig. 7), it can be clearly seen that the amount of C¹⁶O₂ formation is significantly higher for the Pd-rw catalyst. It shows us that the Pd-rw catalyst is easier to be reduced than the other two catalysts. This connection with easy reducibility and methane oxidation activity is consistent with the results of Castellazzi et al. [14].

4. Discussion

In summation, the Pd-rw catalyst showed the best activity in all the isotopic experiments and also the best stability and activity in methane oxidation. To facilitate the comparison the relative activities in methane oxidation (activity of the catalyst divided by lowest activity) were calculated based on the values presented in Table 2. The following values were obtained: Pd-rw: 6, for Pd-w: 2 and for Pd-dry: 1. We used the similar comparison for the exchange and equilibration activities. For pre-oxidized samples in ¹⁶O/¹⁸O exchange at 500 °C the relative activities are for Pd-rw 20, for Pd-w 2 and for Pd-dry 1 (calculated based on the values pre-

sented in Table 3) while that of ¹⁶O/¹⁸O equilibration they are: 5 for Pd-rw, 2 for Pd-w and 1 for Pd-dry (calculated based on the values presented in Table 5). On pre-reduced samples, somewhat different activities in exchange and equilibration were obtained affecting more the ranking of Pd-w and Pd-dry than that of Pd-rw. The relative activities in exchange at 500 °C are: 4 for Pd-rw, 1.2 for Pd-dry and 1 for Pd-w (Table 3) while those of equilibration amount to: 3 for Pd-rw, 1.6 for Pd-dry and 1 for Pd-w (Table 5). To explain these results, several hypotheses related to different activities can be put forward and will be discussed subsequently. These hypotheses are:

- effect of residual Na ions;
- effect of particle size of active phase;
- effect of residual carbonates; and
- possible presence of alumina decoration.

4.1. Possible role of residual Na ions

First of all, one possibility is the residual Na on the catalyst surface that would affect both the rate of CH₄ oxidation and the isotopic exchange [26,27]. No correlation was seen between the exchange and methane oxidation activity and Na amount of different catalyst samples analyzed by ICP. TEM-EDX measurements showed that in the case of Pd-dry, Na is localized close to the Pd-clusters (see Fig. 8), but in the Pd-w sample, no Na was observed and in the case of Pd-rw, the localization of Na was not possible even if it was detected in EDX analysis. Our assumption on the possible enhancing effect of Na located close to Pd is thus not valid or we cannot confirm it.

4.2. Particle size effects

The specific surface area of the Pd-rw catalyst is slightly higher than the other two catalysts, which can slightly improve the rate of exchange, but that cannot explain the increase observed. TEM-EDX measurements showed that the particle size of palladium in all the catalysts is very similar. However, in Pd-dry, that is less active in all the test cases, Pd particles (~2 nm) are forming rather large (100 nm) clusters. The most active Pd-rw catalyst had well-dispersed Pd (~2 nm) on gamma-alumina and no clusters were seen. In the case of Pd-w few 4 nm Pd particles were observed, but most of the particles are assumed to have size less than 1 nm, which is the detection limit of used TEM. This conclusion was made due to results of TEM-EDX measurement where presence of

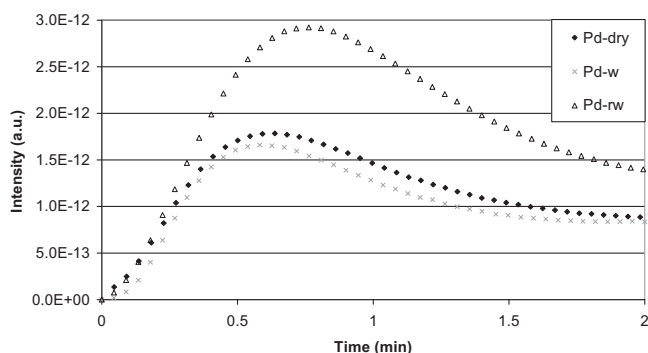


Fig. 7. Appearance of C¹⁶O₂ at the beginning of CH₄ + ¹⁸O₂ experiments at 500 °C over the prepared catalysts.

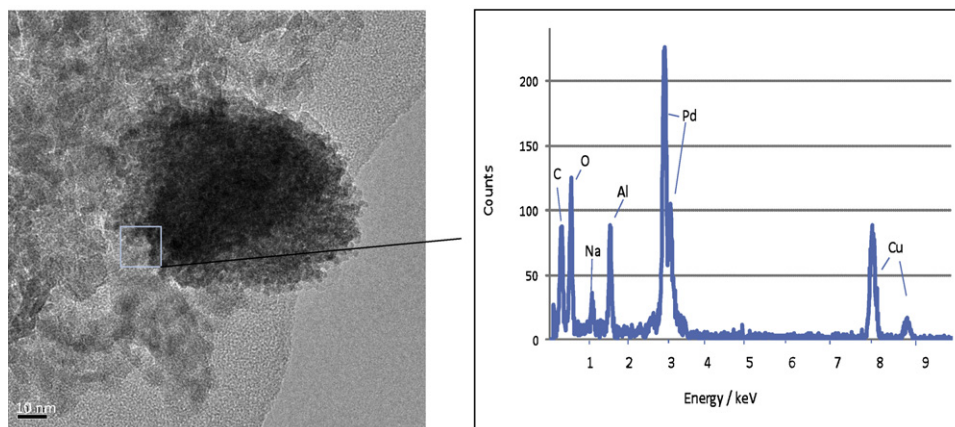


Fig. 8. TEM image of Pd-dry catalyst and example of EDS analysis close to Pd-cluster.

palladium was observed with EDX while no visual evidence of palladium was achieved with TEM (see Fig. 1b). From previous studies [14], it has been seen that a palladium catalyst having a larger particle size is easier to be reduced and therefore it would be more active in methane oxidation as well. In that case the different particle sizes of palladium were 2 nm and 5 nm (based on H_2 chemisorption measurement) and they gave 4–5 times higher TOF for methane oxidation for less dispersed catalysts [14]. This result is in accordance with our notifications concerning methane oxidation activity of the Pd-rw catalyst compared with the Pd-w catalyst, for example, but also the reducibility of the catalyst. In addition to methane oxidation, easy reducibility of PdO seems also to be connected to a good oxygen exchange activity.

4.3. Effect of carbonates on exchange and catalytic activity

It is known that carbonates are able to exchange oxygen rapidly [21]. In addition, it has been seen that an oxidative pre-treatment removes possible residual carbonates from the surface more easily than the reductive pre-treatment [28]. In our case, existence of residual carbonates could be one explanation for the superior performance of the pre-reduced catalyst samples, since a prolonged treatment (repeated oxidation reduction cycles) to remove the carbonates was not done in this case. To confirm this, one experiment was carried out with Pd-rw catalyst by *in-situ* FTIR while doing the repeated pre-treatment, and in fact, it was seen that neither evacuation nor reductive pre-treatment was enough to remove residual carbonates at 400 °C (see Fig. 9, where peaks around 1561 and 1453 are showing the existence of carbonates). Also during the methane oxidation, the CO_2 reaction product can cause formation of carbonates on the surface that will then improve the oxygen exchange reaction.

4.4. Effect of pretreatments on activity in exchange and equilibration

To explain the different activities observed in the two cases, namely, between the similar catalysts that were either *in-situ* pre-oxidized or *in-situ* pre-reduced and the catalysts which preparation procedure was altered (Pd-dry, Pd-w, Pd-rw) a few further hypotheses can be made. We will start with the case of *in-situ* treatment of the catalysts. First of all, we can assume that the re-oxidation of pre-reduced sample at the beginning of the isotopic oxygen exchange reaction is immediate. This would mean, that at $t=0$ the ^{18}O coverage of Pd (pre-reduced) is nearly complete ($\theta_{180} = 1$). Then the following exchange would occur with ^{16}O originating from $\gamma-Al_2O_3$ in the case of oxygen exchange, if there is no

^{16}O available in PdO. In the case of equilibration, ^{16}O can be originated from the gas-phase as well, which is the case of pre-reduced sample, since the consumption of both oxygen isotopomers in the gas-phase are the same and α -value is almost constant. Therefore we can say that participation of ^{16}O from support does not occur significantly. When the methane oxidation was done with $^{18}O_2$, the result showed us that the assumption of very rapid adsorption of $^{18}O_2$ is not probable. If it would be, we should also have observed rapid formation of other isotopomers of carbon dioxide than that of $C^{16}O_2$ at the beginning of the reaction. This result is not supporting the first hypothesis, so we can conclude that the ^{16}O in this case is most likely not originating from $\gamma-Al_2O_3$ but in practice 15 min of pre-reduction is not enough for complete reduction of $Pd^{16}O$.

In the case of a pre-oxidized sample, θ_{180} would be <1 if the exchange between $^{18}O_2$ and $Pd^{16}O$ is slow. When the sample is pre-oxidized, $^{18}O_2$ may exchange with $Pd^{16}O$ forming $Pd^{18}O$ or $^{18}O_2$ can be adsorbed on the surface of $Pd^{16}O$. This possibility includes a hypothesis that the exchange of oxygen between PdO and $\gamma-Al_2O_3$ is more rapid than the exchange between adsorbed oxygen and PdO. It seems that since the exchange rate over the pre-oxidized samples is always lower than over the pre-reduced samples, oxygen in PdO is less reactive in the case of pre-oxidized catalyst. However, in the case of equilibration experiment, both reactions occur, so it seems also that pre-oxidation of the catalyst enables both exchange and equilibration to occur at the same time. Finally, based on current experiments, we cannot make complete conclusion on these phenomena described above.

4.5. Decoration by alumina patches

In connection with the Pd particle size effect (Section 4), a hypothesis on the presence of $\gamma-Al_2O_3$ decoration close/over palladium on certain samples could be set. In this case, the oxygen from gamma-alumina decoration would be more reactive than the oxygen in bulk of gamma-alumina. Some evidence for this exists, namely, the chemisorption measurements show the decrease in dispersion in the order of Pd-dry > Pd-w > Pd-rw, which would mean an increase in particle size. However, TEM measurements showed that the particle size in Pd-dry and Pd-rw are equal (~ 2 nm). This makes us consider the possibility of the presence of alumina decoration/coverage close to Pd-particles that would block the chemisorption of hydrogen but allow exchange of oxygen. Actually, the presence of more reducible palladium in close contact with alumina patches could explain also the better activity in both experimental cases: the differences in activities in the case of different preparation procedures and the differences in activities in the case of different *in-situ* treatments. This hypothesis means

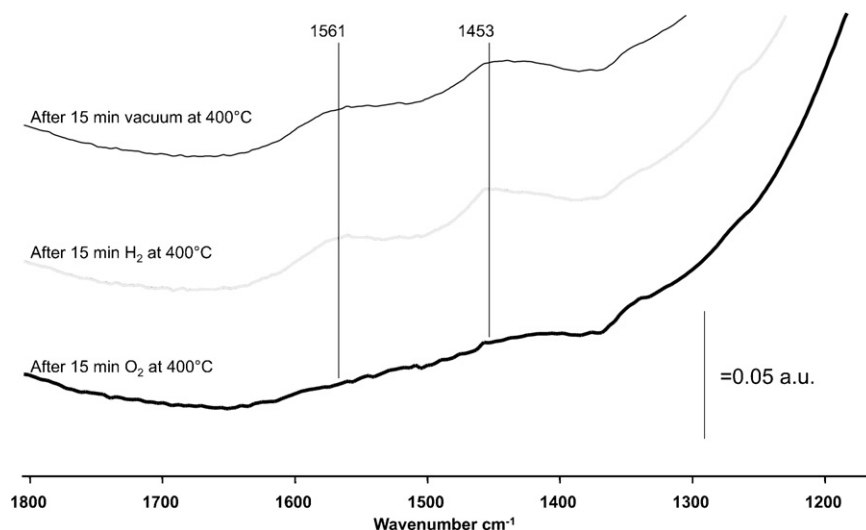


Fig. 9. FTIR spectra of the surface of Pd-w catalyst during the pre-treatment at 400 °C.

that more reducible O–Pd–O–Al sites are present in the cases where reduction is used either in *in-situ* pre-treatment or in connection of catalyst preparation. There exist few previous studies [29,30] where similar situation is observed. Ivanova et al. [29] have characterized Pt and Pd catalysts supported on Al₂O₃ with XRD, UV–vis DRS, HRTEM, H₂-TPR and XPS. They found out that depending on the calcination temperature of the support and catalyst, some formation of Al₂O₃ layer, most likely aluminate thin layer, on the active phase occurred giving a “core–shell” structure. When the catalyst was calcined at higher (up to 1000 °C) temperature less interaction with aluminate and active phase were observed and at the same time Pd⁰/PdO ratio was decreased. They found out also, that the aluminate decoration was stable under treatment of H₂ at temperature range of –15 to 450 °C and under treatment in a reaction mixture of CO and O₂, which would show the formed aluminate to be rather stable. [29] This would mean in our case that the aluminate is not completely removed during the reduction in catalyst preparation-phase or during reductive *in-situ* pre-treatment. However, the differences in the aluminate stability can be caused by the facts that in our case special nitrite-based preparation method was used where strong interactions between active phase and support were avoided while in the studies done by Ivanova et al. the catalysts were prepared by incipient wetness impregnation of palladium nitrate and some of the features observed were suggested to be especially due to strong support-active phase interaction. Unfortunately, these issues should be studied in more detail to confirm completely our hypothesis.

5. Conclusions

The answers to the questions set at the beginning of the paper, namely, what is the reason for the low activity of Pd in oxygen exchange and is there a way to improve it, are the following:

- Palladium's low activity in oxygen exchange is the fact that palladium is in a form of PdO and PdO cannot activate oxygen easily.
- The activation can be improved by preparing a palladium catalyst that is more easily reduced for example by using a reductive pre-treatment or reducer in a gas phase.
- If methane (or other carbon-containing compound) is used as reducing agent, the formation of carbonates may also improve the oxygen exchange.

The correlation was found between the enhanced methane oxidation activity and enhanced oxygen activation that was more pronounced with a catalyst sample that was easier to be reduced. The same activity order in the tested reactions exists independent of the *in-situ* pre-treatment. However, a correlation exists only up to a certain point, since when PdO is completely reduced to Pd⁰, some reoxidation is needed before methane oxidation occurs. This is due to the Mars–van Krevelen type of reaction mechanism. The enhanced activity of *in-situ* pre-reduced samples as well as samples where reduction was used during the preparation is suggested to be due to presence of more reducible palladium ions on the catalyst.

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